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Supporting Information

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# Synthesis and Direct Imaging of Ultrahigh Molecular Weight Cyclic Brush Polymers**

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## Experimental Section

**Materials.** The synthesis and characterization of cyclic catalysts (**SC-5** and **SC-6**) were previously reported.[1] The synthesis and characterization of macromonomers (**NB-PS**, **NB-PLA**, and **NB-P*n*BA**) were previously reported.[2]

**Characterizations.** $^{1}H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ using a Varian Mercury 300 or Varian Inova 500 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ ($\delta$ = 7.27).

Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 $\mu$m mixed-B LS columns (Polymer Laboratories) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used. d*n*/d*c* values of macromonomers were obtained for each injection by assuming 100% mass elution from the columns, and were used for the corresponding brush polymers .

Atomic Force Microscopy (AFM) images were taken using a Nanoscope IV Scanning Probe Microscope Controller (Digital Instruments, Veeco Metrology Group) in tapping mode in air at room temperature using silicon tips (spring constant = 40-50 N/m, resonance frequency = 170-190 kHz, and tip radius of curvature <10 nm). The samples were prepared by spin casting dilute solutions (< 0.01 wt%) in chloroform onto freshly cleaved HOPG for PS brush polymers and mica for PLA brush polymers.

**General procedure for REMP of macromonomers.** In a typical experiment, an oven-dried small vial was charged with 100 mg macromonomer and a stir bar. The vial was then degassed, and the desired amount of degassed, anhydrous solvent ($[M]_0$ = 0.05-0.10 M) was added via syringe under an argon atmosphere to dissolve the macromonomer. A stock solution of catalyst in degassed, anhydrous solvent was prepared in a separate vial. The desired amount of catalyst was injected into the macromonomer solution to initiate the polymerization. The reaction vial was stirred at 55 °C under argon. After the macromonomer conversion stopped increasing (2-5 h), the reaction mixture was cooled in a refrigerator. A small sample was withdrawn for GPC measurement. The rest of the reaction mixture was then diluted with THF and

precipitated into 10 mL stirring MeOH to isolate the polymer. The resulting polymer was dried *in vacuo* at room temperature.

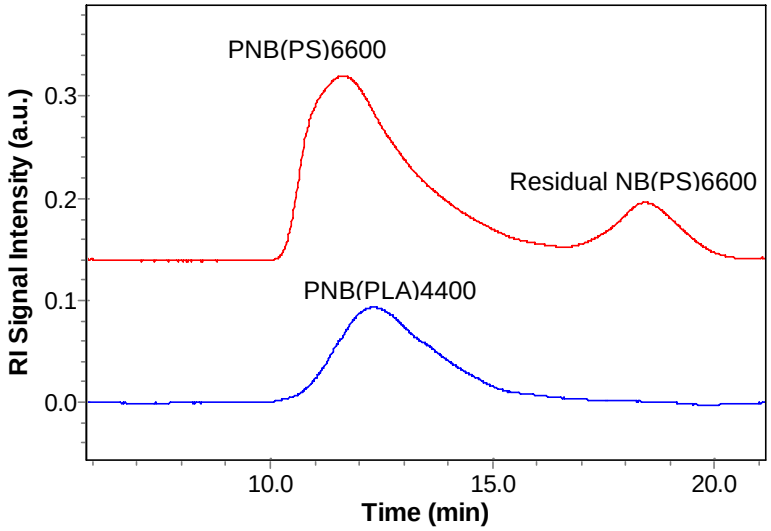


**Figure 1S.** Representative GPC traces of crude cyclic brush polymers.

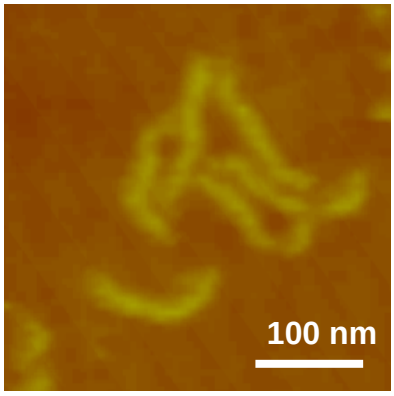


**Figure 2S.** Representative topographic AFM image of a linear brush polymer PNB(PS)6600 synthesized as previously reported.[2] The macromonomer NB(PS)6600 is the same as that used for preparing cyclic brush polymer.

## References

[1] A. J. Boydston, Y. Xia, J. A. Kornfield, I. A. Gorodetskaya, R. H. Grubbs, *J. Am. Chem. Soc.* **2008**, *130*, 12775-12782

[2] Y. Xia, J. A. Kornfield, R. H. Grubbs *Macromolecules* **2009**, *42*, 3761-3766.